

III.A.21 Electrically Conductive, Corrosion-Resistant Coatings through Defect Chemistry for Metallic Interconnects

Anil V. Virkar

University of Utah

Department of Materials Science & Engineering

122 S. Central Campus Drive

Salt Lake City, UT 84112

Phone: (801) 581-5396; Fax: (801) 581-4816; E-mail: anil.virkar@m.cc.utah.edu

DOE Project Manager: Lane Wilson

Phone: (304) 285-1336; E-mail: Lane.Wilson@netl.doe.gov

Objectives

- To synthesize and characterize electronically conductive coating materials with ultra-low oxygen diffusion coefficient, using site-specific doping and through fundamental understanding of defect chemistry, for application on metallic interconnects in intermediate temperature (800°C) solid oxide fuel cells (SOFCs).
- To apply the coatings on low thermal expansion, relatively inexpensive stainless steels and other alloys, and investigate oxidation kinetics in air and fuel atmospheres.
- To conduct preliminary short stack (4-cell) test using 5 cm x 5 cm active area cells to validate ex-situ results.
- To initiate work on the development of low-cost processes for the deposition of the coatings on metallic interconnects.
- To offer coated interconnect foils to the Solid State Energy Conversion Alliance (SECA) vertical teams under suitable confidentiality agreements.

Approach

- Conduct literature search to identify suitable perovskite and non-perovskite materials exhibiting high electronic conductivity but very low oxygen ion conductivity. Non-perovskite materials of interest include spinels and bronzes.
- Synthesize perovskite oxides with transition element on the B-site, with site-specific doping to suppress oxygen vacancy concentration.
- Fabricate sintered bars and discs of the materials. Sintered bars will be used for the measurement of total conductivity as a function of temperature. Discs will be used for measuring ionic conductivity using electron-blocking electrodes.
- Deposit thin coatings of the materials on stainless steels and nickel-based alloy foils, and investigate oxidation kinetics.
- Conduct theoretical analysis of oxidation kinetics of coated and pristine alloys.
- Develop a method for the measurement of area-specific resistance (ASR), and apply it to the foils oxidized under various conditions.

Accomplishments

- Identified a number of materials with low oxygen ion conductivity (possibly lower than 10^{-7} S/cm at 800°C) by taking into account ionic size effect.
- Fabricated LaMnO₃-based materials with dopant level as high as 20% on the B-site to suppress oxygen ion conductivity.

- Measured total conductivity over a temperature range from room temperature to 800°C, and measured oxygen ion conductivity at 800°C.
- Sputter-deposited 1- and 3-micron coatings of various materials on Haynes 230, Inconel 718, and SS 430.
- Conducted preliminary oxidation studies in air up to 28 days at 800°C.
- Examined oxide scale formed and measured its thickness on coated and pristine materials for oxidation times up to 28 days.
- Measured total ASR of the coated and pristine samples after oxidation. It was observed that the pristine samples exhibited significant oxidation. However, even samples with as small as 1 micron coating were highly resistant to oxidation.

Future Directions

- Deposit coatings of thicknesses up to 5 microns on both sides of the foils, and evaluate performance in air, fuel, and dual atmospheres.
- Measure ASR on coated and pristine foils subjected to various oxidative treatments.
- Develop theoretical models for oxidation kinetics and verify the models experimentally.
- Conduct a short stack test with the best coating material, as determined by ex-situ oxidation studies.

Introduction

Planar SOFC stacks are preferred over their tubular counterpart due to compact design, higher power and energy density, and projected lower cost. However, planar SOFC stacks require interconnects or bipolar plates to keep fuel and oxidants separate and to electrically connect adjacent cells. From the standpoint of cost and ruggedness, metallic interconnects are preferred. However, metallic interconnects of choice are stainless steels or nickel-chromium-based alloys, which are prone to oxidation. The oxide scale formed increases the ASR, which adversely affects the SOFC performance and efficiency and thus, in balance, also adversely affects the cost. The potential remedy is the development of either baseline alloys that are oxidation-resistant, or suitable coating materials which can suppress oxidation kinetics. From the standpoint of cost and practicality, the preferred approach is the development of suitable coating materials.

To date, several coating materials have been tried, with varying degrees of success. The approach, however, has not been systematic, and it has relied on trial and error. As a result, most of the coatings used to date were very thick (several or several tens of microns). This increases the potential for spalling, which is undesirable. The approach selected in this work is based on fundamental chemistry of materials and has the potential to

develop coatings that are adherent and very thin (typically less than 5 microns, and maybe as thin as 1 micron), and yet can suppress oxidation kinetics to greater than 40,000 hours of operating life.

Approach

Possible coating materials are perovskites with a transition metal, capable of exhibiting multiple valence states. An example is LaMnO_3 . The approach involves doping a material such as LaMnO_3 (LM) with suitable elements, which tends to suppress oxygen vacancy concentration, without significantly reducing electronic defect concentration. Powders of various coating materials, doped appropriately, are made. Samples of the materials are made by sintering. Two types of electrical tests are performed: (a) measurement of total electrical conductivity and (b) measurement of oxygen ion conductivity using blocking electrodes. Thin coatings (1 to 5 microns) are then deposited on foils of various alloys. For the initial investigation, Haynes 230, Inconel 718, and SS 430 were the alloys selected. The coated and uncoated foils are subjected to air and fuel for various periods of time and over a range of temperatures, up to ~800°C. Samples are oxidized for various periods of time, up to a maximum of six months. The oxide scale thickness is measured using scanning electron microscopy (SEM). The observed kinetics of oxidation is compared with the theoretical models developed. The ASR of the samples is also measured as a

function of time of oxidation, with measurements conducted over a range of temperatures. Finally, a short stack will be tested using coated interconnects exhibiting the best properties.

Results

Identified a number of possible perovskite and non-perovskite materials with potential for good electronic conductivity and low oxygen ion conductivity. This was achieved using crystal chemistry considerations. Criteria based on ionic size were used to identify materials with low oxygen vacancy mobility. Criteria based on defect chemistry were used to identify materials with low oxygen vacancy concentration.

Samples of perovskite and non-perovskite structures were fabricated in the form of discs and bars. Total electrical conductivity, which is mainly electronic, was measured over a range of temperatures using a four-probe DC method. Figure 1 shows the total conductivity measured as a function of temperature (Arrhenius plot) on several prospective coating materials. The lowest measured value was ~ 4 S/cm, which shows that the ASR is expected to be low.

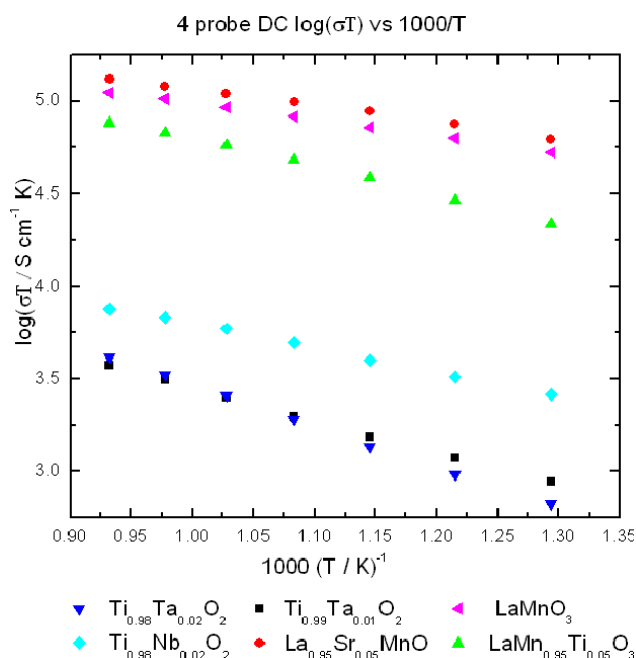


Figure 1. Arrhenius plots of conductivity of a number of coating materials. The total conductivity is predominantly electronic, with oxygen ion conductivity orders of magnitude lower.

Tri-layer, sandwich samples comprising a disc of the material of interest sandwiched between two YSZ discs were fabricated. The YSZ discs serve as electron-blocking electrodes. It is important that the interfaces are well-formed, free of defects such as cracks. Figure 2 shows an SEM image of one of the

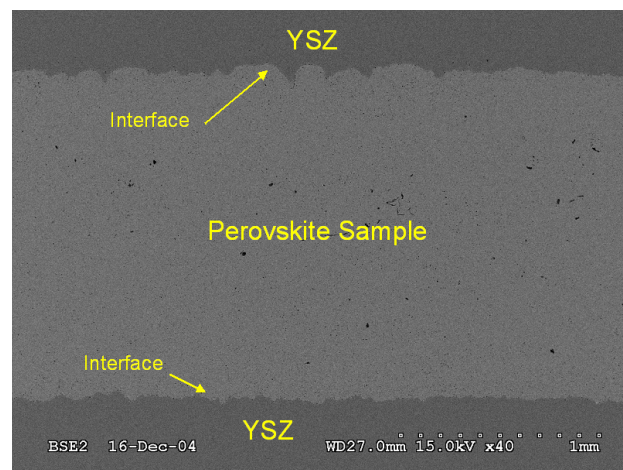


Figure 2. An SEM image of the tri-layer structure comprising a perovskite sample sandwiched between two YSZ discs, the latter serving as electron-blocking electrodes. Note the well-bonded interfaces.

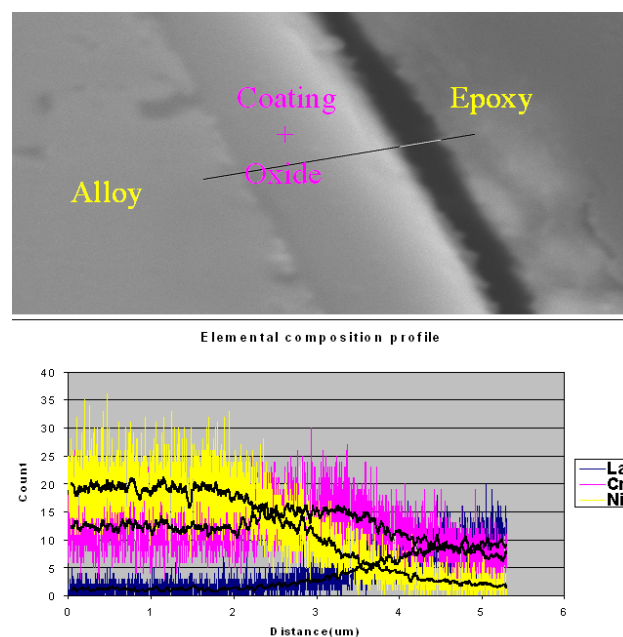


Figure 3. Composition profiles of elements La, Cr, Ni across metal-oxide layer-coating interface. Metal on left side, coating on right side, and oxide layer in the center.

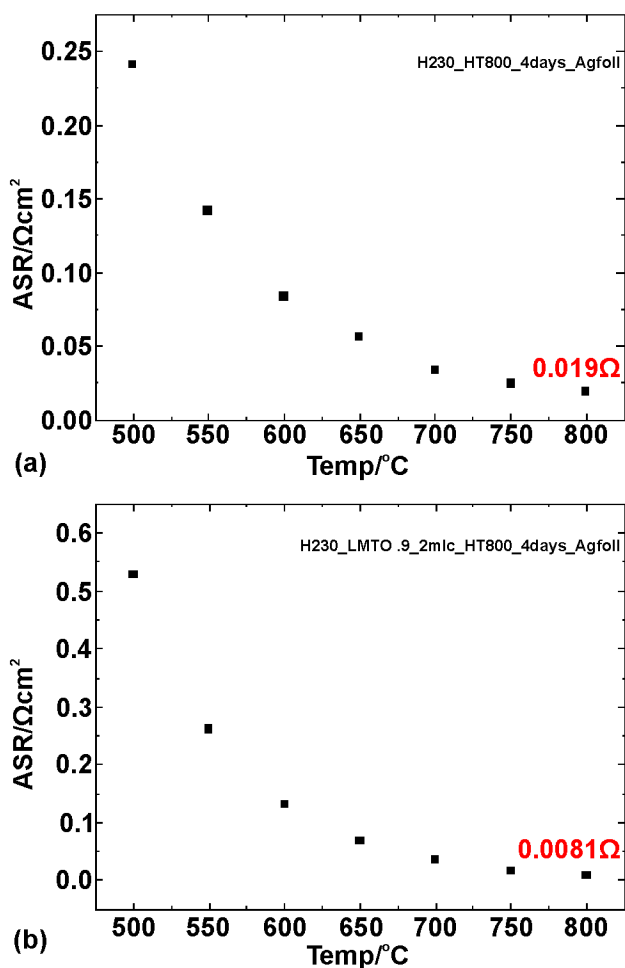


Figure 4. Plots of ASR vs. temperature for (a) Uncoated H230 alloy foil, (b) LMT0.9 coated H230 alloy foil oxidized at 800 $^{\circ}\text{C}$ for 4 days. The ASR values at 800 $^{\circ}\text{C}$ are highlighted in red. Note that the ASR of the coated alloy foil is less than half that of the uncoated foil at 800 $^{\circ}\text{C}$.

tri-layer samples. Using the blocking electrode method, preliminary measurements of oxygen ion conductivity have been made. The lowest value measured at 800 $^{\circ}\text{C}$ is $\sim 10^{-7}$ S/cm, which is satisfactory. Experiments on other coating materials are underway to identify materials with even lower oxygen ion conductivity.

Successfully deposited a number of coating materials on foils of several alloys. The thickness of the coatings was varied between 1 and 3 microns.

Coated and pristine samples were subjected to oxidation studies. It was observed that coated foils exhibited very low oxidation kinetics. The oxide scale was typically about a micron in thickness even after three weeks at temperature. The oxide scale formed under the coating. The coating was strongly adherent, especially on the nickel-based alloy foils. Figure 3 shows an SEM image of a foil of H230 with a protective coating, and an oxide scale formed under the coating. Also shown in the figure is the chemical analysis conducted using energy dispersive x-ray.

ASR was measured over a range of temperatures on as-received foils and coated foils after oxidative treatments. Figure 4 shows the results of ASR measurements on uncoated and coated H230 foils after oxidation in air at 800 $^{\circ}\text{C}$ for 4 days. It is seen that the coated foil exhibits ASR at 800 $^{\circ}\text{C}$ less than half that of the uncoated foil.

Conclusions

Defect chemistry plays a major role in oxygen ion transport through oxides, and thus determines the suitability of a given material as a coating. Coating materials based on LaMnO_3 (perovskite) and TiO_2 (non-perovskite) were successfully made.

Electronic and ionic conductivities of coating materials are in accord with defect chemistry, and that defect chemistry provides a scientific basis for the design of oxidation-resistant coatings.

High-quality, strongly adherent coatings can be sputter deposited. The resulting foils exhibit improved oxidation resistance over the baseline foils. Even after several days at 800 $^{\circ}\text{C}$, the coating continues to remain well-bonded.

Coated foils also exhibit much lower ASR as compared to pristine foils.

